A Hamilton-Jacobi Formalism for Thermodynamics

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Abstract

We show that classical thermodynamics has a formulation in terms of Hamilton-Jacobi theory, analogous to mechanics. Even though the thermodynamic variables come in conjugate pairs such as pressure/volume or temperature/entropy, the phase space is odd-dimensional. For a system with n thermodynamic degrees of freedom it is $2n + 1$-dimensional. The equations of state of a substance pick out an n-dimensional submanifold. A family of substances whose equations of state depend on n parameters define a hypersurface of co-dimension one. This can be described by the vanishing of a function which plays the role of a Hamiltonian. The ordinary differential equations (characteristic equations) defined by this function describe a dynamical system on the hypersurface. Its orbits can be used to reconstruct the equations of state. The 'time' variable associated to this dynamics is related to, but is not identical to, entropy. After developing this formalism on well-grounded systems such as the van der Waals gases and the Curie-Weiss magnets, we derive a Hamilton-Jacobi equation for black hole thermodynamics in General Relativity. The cosmological constant appears as a constant of integration in this picture.

1 Introduction

General Relativity is surprisingly similar in many ways to Thermodynamics. It predicts an irreversibility in the dynamics of black holes: the area of the horizon must increase. Since we cannot see the interior of a black hole, they carry an entropy which must be proportional to this area. The analogy suggests that GR is the average over some as yet unknown microscopic degrees of freedom.

The situation is analogous to that with the theory of gases at the end of the nineteenth century. It was clear that the kinetic theory of gases gave a good derivation of the ideal gas law and through the work of Boltzmann, a possible derivation of thermodynamic laws from the first principles of mechanics. Yet, it was not known then what the value of Boltzmann's constant was, or equivalently, how big molecules are. Yet, van der Waals was able to deduce a simple equation for the departure of a gas from ideal by simple considerations of molecular dyamics. In a similar way, it might be possible to test microscopic theories of gravity by their implications on the thermodynamics of black holes or of the universe. We find already an intriguing connection between black hole thermodynamics and the cosmological constant.

This motivation led us to questions about thermodynamics that turned out to be of independent interest . In particular, we found a dynamical system on the thermodynamic phase space that is analogous to classical mechanics but is still quite different. The 'time' variable of this evolution of the thermodynamic variables is related to, but is not always the same as, entropy. Although many of the ingredients of our theory were known in the nineteenth century, this particular form of thermodynamics appears to be still new. We have tried to make the paper self-contained by reviewing some of the background material on mechanics (section 1), thermodynamics of gases (section 2) and magnets (section 3) and contact geometry (section 4). The erudite reader could skip ahead to sections 2.3, 3.3, 5 and 6 for the new material.

1.1 The Three Classical Disciplines

Three important disciplines of classical physics are Mechanics, Ray Optics and Thermodynamics. The work of Hamilton and Jacobi showed that Mechanics and Ray optics had a very similar structure: they can both be formulated in terms of the Hamilton-Jacobi (or eikonal) equation. We now understand why that is so: they are both approximations to wave theories in the limit of short wave length.

Let us invert history and start with the wave equations of optics and quantum mechanics[1, 2]

$$\frac{n^2(x)}{c^2}\frac{\partial^2}{\partial t^2}\phi = \nabla^2\phi, \quad i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi \tag{1}$$

If we put $\phi = e^{\frac{iS}{\lambda}}, \psi = e^{\frac{iS}{\hbar}}$ these become in the limit $\lambda \to 0, \hbar \to 0$:

$$\frac{n^2(x)}{c^2}\left(\frac{\partial S}{\partial t}\right)^2 = (\nabla S)^2, \quad \frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2m} + V(x) \tag{2}$$

These are the Eikonal and Hamilton-Jacobi equations. The phase of the wave is constant on the wave front (the surface $S = $ constant) and varies most rapidly along the vector ∇S which is normal to the wavefront. The wave can be thought of as propagating along the ray that solves the ODE $\frac{dx}{dt} = \nabla S$.

1.2   Hamilton's Equations

Thus ∇S is proportional to the wavenumber (momentum). We can identify also $\frac{\partial S}{\partial t}$ with frequency (energy) up to a constant. A Hamilton-Jacobi equation of the form

$$H\left(x, \nabla S\right) = \frac{\partial S}{\partial t} \tag{3}$$

is equivalent to the system of ordinary differential equations that determine the rays[3]

$$\frac{dx}{dt} = \frac{\partial H}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H}{\partial x}. \tag{4}$$

These in turn are equivalent to Newton's laws of mechanics (or Snell's law of refraction).

Position and momentum appear symmetrically in the above equations. In fact there is a much bigger symmetry. Any observable $F(x, p)$ generates a one-parameter family of co-ordinate transformations through Hamilton's equations. These are the canonical transformations generated by that observable. Time evolution is simply the canonical transformation generated by the energy (Hamiltonian) function. Momentum generates translations, angular momentum generates rotations etc. Observables come in conjugate pairs generating translations on each other[2].

1.3   Classical Thermodynamics

In this paper we will show that thermodynamics is a third facet of this classical framework. Gibbs [4] realized that the basic law of thermodynamics, combining the first and second laws, has a geometric meaning[4]. The theory of differential forms was developed by Pfaff, Caratheodory and others to give his insight an elegant mathematical formulation. Chandrashekhar [5] gives a rare treatment of this subject in a textbook. An analogy of thermodynamics with mechanics and optics is mentioned occasionally [6, 8, 9, 10]. The most detailed geometrical formulation is in the review article Ref. [12]. It is shown there that a hypersurface in a contact manifold defines a dynamical system.

But the physical meaning of this dynamics appears not to be clarified anywhere[1]. What is the meaning of such a hypersurface in thermodynamics? It is certainly not the submanifold defined by the equation of state of a material, as

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[1]This analogy with mechanics was noticed in Ref. [9], but it is not as perfect as implied there. In particular, because the thermodynamic phase space is odd dimensional (see below), the correct formalism uses contact geometry and Legendre transformation rather than symplectic geometry and Poisson brackets.

it has the wrong dimension. (More precisely, it is not a Lagrangian submanifold. See below). What is the Hamilton-Jacobi equation of thermodynamics for some familiar systems like gases or magnets? What is the meaning of the 'time' variable in this dynamics? What are the implications for the thermodynamics of black holes? These are the questions we will begin to address in this paper. After understanding these down to earth system we will turn to the dynamics of the simplest black hole.

2   Thermodynamics of Gases

To be concrete let us consider the most familiar thermodynamic system, a gas with a fixed number of molecules. It has five thermodynamic variables U, T, S, P, V: the internal energy, temperature, entropy, pressure and volume. S, U, V are *extensive variables*; i.e., are proportional to the size of the system. P, T are intensive: they do not scale with the size of the system. Two subsystems are in equilibrium if they have equal values for the intensive variables.

Extensive and intensive variables come in conjugate pairs such as pressure/volume or temperature/entropy. Yet there are always an odd number of variables. This can be seen in the first law of thermodynamics which is a condition on the infinitesimal variations of these quantities:

$$\alpha \equiv dU - TdS + PdV = 0. \tag{5}$$

The conjugate pairs appear together as PdV or TdS, except for internal energy which has no conjugate.

An equivalent form would be

$$dS - T^{-1}dU - \tilde{P}dV = 0 \tag{6}$$

where $\tilde{P} = \frac{P}{T}$. Indeed any variable can be chosen to be in the privileged position as the 'fundamental variable' in the first term, with unity as the conjugate. This symmetry resolves the apparent contradiction of having an odd variables, while at the same that variables come in pairs. α is only determined modulo multiplication by a non-zero function: only its kernel (zero set) has a physical significance.

Equivalent formulations of the first law are

$$d[U + PV] - VdP - TdS = 0, \quad d[U - TS] + PdV + SdT = 0 \tag{7}$$

etc., in which the positions of some of the extensive and intensive variables are switched. These transformations are analogous to the canonical transformations of classical mechanics and are called Legendre transformations. More on this later.

2.1   The Ideal Gas

The particular two dimensional surface corresponding to each material is given by three equations of state to be satisfied among the variables (T, P, s, u, v). For

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example, a monatomic ideal gas satisfies the laws

$$Pv = T, \quad u = \frac{3}{2}T \tag{8}$$

where $V = nRv$ is the volume of the gas, $U = nRu$ the internal energy, n is the number of moles of the gas in the sample and $R \approx 8.3\text{JK}^{-1}\text{mol}^{-1}$ is the gas constant. The remaining relation needed to fix the two dimensional surface of the ideal gas is obtained by integrating the differential equation $\alpha = 0$. This gives the entropy [2]:

$$ds - \frac{P}{T}dv - \frac{1}{T}du = 0 \Rightarrow s = \log\left[u^{\frac{3}{2}}v\right]. \tag{9}$$

This holds up to an additive constant of integration; i.e., independent of u, v.

Conversely, once this 'fundamental relation' between extensive variables is given the intensive variables are determined by

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u}\right)_v, \quad \frac{P}{T} = \left(\frac{\partial s}{\partial v}\right)_u \tag{10}$$

which are the other equations of state.

2.2   van der Waals Gases

A simple model of a non-ideal gas is due to van der Waals[14]:

$$P = \frac{T}{v - b} - \frac{a}{v^2} \tag{11}$$

where a, b are constant parameters. We can regard b as the volume excluded because of the finite size of the molecules. The constant a measures the strength of the short range attraction among the molecules.

Let us now find the entropy:

$$\begin{aligned} ds &= \frac{P}{T}dv + \frac{du}{T} \\ &= \frac{dv}{v - b} + \frac{du - \frac{a}{v^2}dv}{T} \end{aligned} \tag{12}$$

Thus T is an integration factor which must make the last term an exact differential. A moments thought gives

$$T = \frac{2}{3}\left[u + \frac{a}{v}\right]. \tag{13}$$

We fix the constant of integration by noting that the low density limit $v \to \infty$ must be the ideal gas. Thus,

$$s = \log\left[(v - b)\left(u + \frac{a}{v}\right)^{\frac{3}{2}}\right] \tag{14}$$

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[2] $S = nRs$, where n is the number of moles of the gas and R the gas constant. We will find it useful similarly to define 'specfifor all extensive variables $S = nRs, V = nRv, U = nRu, M = nRm$ etc. The gas constant is put in to simplify later formulas.

To check:

$$\frac{P}{T} = \left(\frac{\partial s}{\partial v}\right)_u = \frac{1}{v-b} - \frac{3a}{2v^2}\frac{1}{u+\frac{a}{v}}, \quad \frac{1}{T} = \left(\frac{\partial s}{\partial u}\right)_v = \frac{3}{2}\frac{1}{u+\frac{a}{v}} \tag{15}$$

from which it follows that

$$P = \frac{T}{v-b} - \frac{a}{v^2}. \tag{16}$$

Now we can eliminate the two parameters a, b from the three equations (11,13,16) to get an equation relating the thermodynamic variables:

$$\left[\frac{P}{T}v - \frac{1}{T}u + \frac{3}{2}\right]^2 T^{-3} = \frac{27}{8}v^2 e^{-2s} \tag{17}$$

This is the hypersurface in the thermodynamic phase space describing the whole family of van der Waals gases. We want to find such an equation for all the examples of thermodynamic systems we study.

2.3 Hamilton-Jacobi equation for van der Waals gases

From the equation (17) we can now recover the equations of state of the van der Waals gases. In the picture in which s is the thermodynamic potential and u, v are the co-ordinates we can put in for their conjugates

$$T^{-1} = \left(\frac{\partial s}{\partial u}\right)_v, \quad \frac{P}{T} = \left(\frac{\partial s}{\partial v}\right)_u \tag{18}$$

to get the first order PDE

$$\left[v\frac{\partial s}{\partial v} - u\frac{\partial s}{\partial u} + \frac{3}{2}\right]^2 \left(\frac{\partial s}{\partial u}\right)^3 = \frac{27}{8}v^2 e^{-2s}. \tag{19}$$

This is the Hamilton-Jacobi equation of the thermodynamics of van der Waals gases. The complete integral of this equation (in the sense of Ref.[3]) will have two undetermined parameters. This is exactly (14).

3 Magnetic systems

For a magnetic system, the analogue of pressure is the applied magnetic field B and its conjugate variable is the magnetization M. The law of thermodynamics becomes[3]

$$\alpha \equiv dU - TdS - BdM = 0. \tag{20}$$

The equations of state that determine the two dimensional surface of a magnetic material is known if we know $S(U, M)$ or the Gibbs potential $G(B, T)$. We expect that the entropy will decrease with increasing magnetization as the

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[3]For simplicity we consider only one component of the magnetic field and magnetization. When the magnetic susceptibility is isotropic this is sufficient.

system is getting more ordered: its molecules are more aligned. Again by considering one mole of the paramagnetic substance, the thermodynamic law becomes

$$ds = \frac{1}{T}du - bdm, \quad b = \frac{B}{T}. \tag{21}$$

where, as before,

$$S = nRs, \quad M = nRm, \quad U = nRu \tag{22}$$

and n is the number of moles of the magnetic material.

3.1 The Ideal Paramagnet

The magnetic analogue of an ideal gas is an ideal paramagnet, consisting of dipoles that don't interact with each other, only with an applied external field [7]. Thus the internal energy of the magnets is independent of m, same as what it would have been in the absence of magnetism :

$$u = u_0(T). \tag{23}$$

In these variables b, m, T , temperature 'decouples' from the magnetic variables and we can treat the two degrees of freedom independent of each other.

$$ds = -bdm + \frac{1}{T}du_0(T). \tag{24}$$

Each material has an equation of state that relates b to m . We would expect that m is an odd function of b, which tends to some finite limiting value m_0 as $b \to \infty$: when all the molecular magnetic moments have been aligned. A simple model that captures this idea would be

$$m = m_0 f\left(bm_0\right) \tag{25}$$

for a constant m_0 and an odd function $f(y)$. The function $f(y)$ should tend to ± 1 as $y \to \pm\infty$. Also, $f(y) \approx y + \mathrm{O}(y^3)$ for small y . If g is the inverse function of f, so that $g(f(y)) = y$,

$$b = \frac{1}{m_0}g\left(\frac{m}{m_0}\right). \tag{26}$$

The magnetic part of the entropy would then be given by $\frac{\partial s_1}{\partial m} = -b$ so that

$$s_1(m) = -\int_0^{\frac{m}{m_0}} g(x)dx. \tag{27}$$

Thus

$$s = s_1\left(m\right) + s_0(T) \tag{28}$$

where $\frac{ds_0(T)}{dT} = \frac{1}{T}\frac{du_0(T)}{dT}$.

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For example, the case of spin $\frac{1}{2}$ magnetic moments

$$f(y) = \tanh y, \ g(x) = \frac{1}{2}\log\left(\frac{1+x}{1-x}\right), \ s_1(x) = -\frac{1}{2}x\log\left(\frac{1+x}{1-x}\right) - \frac{1}{2}\log[1-x^2].$$

(29)

But a simpler choice leading to more explicit answers is

$$f(y) = \frac{y}{\sqrt{1+y^2}}, \quad g(x) = \frac{x}{\sqrt{1-x^2}}, \quad s_1(x) = \sqrt{1-x^2} - 1.$$

(30)

These two functions $f(x)$ and $g(x)$ are similar enough to $\tanh x$ and $\operatorname{arctanh} x$ that the simpler choice already gives us a good idea of what is going on. The simplest model for the non-magnetic part of the internal energy would be that the molecules carrying the magnetic moment are oscillating around the vertices of a lattice. If there are r such oscillatory degrees of freedom, equipartition of energy gives

$$u_0(T) = \frac{r}{2}T.$$

(31)

Thus

$$s_0(T) = \frac{r}{2}\log T.$$

(32)

3.2   Curie-Weiss Theory

Just as the van der Waals theory gives a simple model for non-ideal gases, the Curie-Weiss theory gives a simple model for ferromagnetism. Each spin is thought of as interacting with a local magnetic field that is the sum of the applied field and a constant multiple of the average of all the other spins. Thus each model of ideal paramagnet can be turned into a Curie-Weiss model for ferromagnetism. The formula for magnetization is modified to the implicit (self-consistent) formula

$$m = m_0 f\left(m_0 b + \frac{T_c}{T}\frac{m}{m_0}\right)$$

(33)

The parameter T_c (the Curie temperature) measures the strength of the interactions of the magnets. When $b = 0$, the solution remains $m = 0$ as long as $T < T_c$. If $T > T_c$, there can be spontaneous magnetization even when $b = 0$. By writing the equation of state as

$$b = \frac{1}{m_0}g\left(\frac{m}{m_0}\right) - \frac{T_c}{T}\frac{m}{m_0^2}$$

(34)

and requiring that

$$ds = -b\,dm + \frac{du}{T}$$

(35)

be an exact differential, we get

$$u(m,T) = -\frac{1}{2}T_c\left(\frac{m}{m_0}\right)^2 + u_0\left(T\right), \quad s = s_1\left(\frac{m}{m_0}\right) + s_0(T)$$

(36)

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where u_0 and s_1 are the same functions as for the ideal paramagnet.

We can now eliminate the parameters m_0, T_c to get a relation between s, T, b, u, m that characterizes the Curie-Weiss models. First of all,

$$mb = xg(x) - x^2 T_c \frac{1}{T}, \quad x = \frac{m}{m_0}. \tag{37}$$

We eliminate T_c using ,

$$u = u_0(T) - \frac{1}{2} x^2 T_c \tag{38}$$

so that

$$mb = xg(x) + 2 \frac{u - u_0(T)}{T}. \tag{39}$$

If we define the functions h and j by

$$h(s_1(x)) = x, \quad j(y) = h(y)g(h(y)) \tag{40}$$

we get

$$x = h(s - s_0(T)) \tag{41}$$

and

$$mb = j(s - s_0(T)) + 2 \frac{u - u_0(T)}{T}. \tag{42}$$

Thus the two functions $s_0(T)$ and $g(x)$ characterize the mean field model, recalling

$$u_0(T) = \int_0^T T ds_0(T), \quad s_1(x) = -\int_0^x g(x)dx. \tag{43}$$

We can get an explicit form of this constraint with the simple models

$$u_0(T) = \frac{r}{2} T, \quad s_1(x) = 1 - \sqrt{1 - x^2} \Rightarrow \tag{44}$$

$$g(x) = \frac{x}{\sqrt{1 - x^2}}, \quad h(y) = \sqrt{1 - (y - 1)^2}, \quad j(y) = \frac{1}{y} - y, \tag{45}$$

$$mb = \frac{1}{s - s_0(T)} - [s - s_0(T)] + 2 \frac{u - u_0(T)}{T} \tag{46}$$

And finally

$$mb = \frac{1}{s - \frac{r}{2} \log T} - [s - \frac{r}{2} \log T] + 2 \frac{u}{T} - r. \tag{47}$$

3.3 Hamilton-Jacobi Theory for Curie-Weiss Magnets

It is simplest to use T, m as the thermodynamic variables. Then the law of thermodynamics becomes

$$d\Xi = -SdT + BdM, \quad \Xi = U - TS \tag{48}$$

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where Ξ is the Helmholtz Free energy. Defining $\Xi = nR\xi$ as before

$$d\xi = -sdT + Tbdm, \quad s = -\left(\frac{\partial \xi}{\partial T}\right)_m, \quad b = \frac{1}{T}\left(\frac{\partial \xi}{\partial m}\right)_T. \qquad (49)$$

The Hamilton-Jacobi equation becomes, with $\eta = \xi + \frac{r}{2T}$,

$$\left[\frac{m}{T}\frac{\partial \eta}{\partial m} - \frac{\partial \eta}{\partial T} - \frac{2r}{T^2} + 2\frac{\eta}{T} - r\right]\frac{\partial \eta}{\partial T} = 1. \qquad (50)$$

Again we can find the general solution with two arbitrary parameters which will give the equations of state.

4   Contact Geometry

We can abstract out of the above a mathematical structure that captures the essence of thermodynamics.

Consider a local patch with co-ordinates $(q^0, q^1 \cdots, q^n, p_1, \cdots p_n)$ of a manifold with dimension $2n + 1$. A *contact structure* in this patch is given by the one-form

$$\alpha \sim dq^0 - p_i dq^i, \cdots i = 1, \cdots n \qquad (51)$$

up to multiplication by a non-zero function. That is, we are to regard α and $f\alpha$ (for a non-zero function f) as equivalent. It is the vanishing of the infinitesimal variations that defines a contact structure.

We can think of

$$dq^0 - p_i dq^i \qquad (52)$$

as the condition for maximizing (or minimizing) some quantity q^0 subject to the constraint that some others q^i are held constant; the p_i are the Lagrange multipliers that enforce the constraints. Such problems arise not only in statistical mechanics and thermodynamics, but also in other areas of physics and even in economics[10, 11].

There are many other co-ordinate systems in which also the contact form (up to multiplication by a non-zero scalar) has the above canonical expression. From

$$f[dq^0 - p_i dq^i] = dQ^0 - P_i dQ^i \qquad (53)$$

we get the conditions

$$\frac{\partial Q^0}{\partial p_i} = P_j\frac{\partial Q^j}{\partial p_i}, \quad -\frac{\partial Q^0}{\partial q^i} + P_j\frac{\partial Q^j}{\partial q^i} = p_i\left[\frac{\partial Q^0}{\partial q^0} - P_j\frac{\partial Q^j}{\partial q^0}\right] \qquad (54)$$

$$f = \frac{\partial Q^0}{\partial q^0} - P_j\frac{\partial Q^j}{\partial q^0} \qquad (55)$$

Transformations $(q^0, q^i, p_i) \rightarrow (Q^0, Q^i, P_i)$ that satisfy these conditions are called *Legendre transformations*.

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A contact manifold is a union of co-ordinate patches such that the transformations among co-ordinates defined at the intersections are Legendre transformations. In most cases the contact manifold of interest is just R^{2n+1} with the standard contact form above. But there are exceptions: a superconducting circuit with a Josephson junction has $R^4 \times S^1$ as the thermodynamic phase space[15]. Even on R^3, there are contact structures that are not equivalent to the standard one; i.e., that need several patches to cover R^3. But it is not clear yet whether they are of interest physically. In any case, we will be content with a local description in this paper.

4.1   Generating Functions of Legendre Transformations

An infinitesimal Legendre transformation

$$q^0 \to q^0 + tV^0, \quad q^i \to q^i + tV^i, \quad p_i \to p_i + tV_i, \quad |t| << 1 \qquad (56)$$

defines a vector field

$$V = V_0 \frac{\partial}{\partial q^0} + V^i \frac{\partial}{\partial q^i} + V_i \frac{\partial}{\partial p_i} \qquad (57)$$

whose components satisfy the infinitesimal version of the above condition:

$$\frac{\partial V^0}{\partial p_i} = p_j \frac{\partial V^j}{\partial p_i}, \quad -\frac{\partial V^0}{\partial q^i} + p_j \frac{\partial V^j}{\partial q^i} + V_i = p_i \left[\frac{\partial V^0}{\partial q^0} - p_j \frac{\partial V^j}{\partial q^0} \right] \qquad (58)$$

$$f = \frac{\partial V^0}{\partial q^0} - p_j \frac{\partial V^j}{\partial q^0} \qquad (59)$$

After a little work we can see that all the components are expressible in terms of the single function $F = p_j V^j - V^0$:

$$V^j = \frac{\partial F}{\partial p_j}, V_i = - \left[\frac{\partial F}{\partial q^i} + p_i \frac{\partial F}{q^0} \right], V^0 = p_i \frac{\partial F}{\partial p_i} - F. \qquad (60)$$

Thus an infinitesimal Legendre transformations is determined by a single function F, called its *generating function*.

Conversely, given a function F, define the vector field

$$V_F = \left[p_i \frac{\partial F}{\partial p_i} - F \right] \frac{\partial}{\partial q^0} - \left[\frac{\partial F}{\partial q^i} + p_i \frac{\partial F}{\partial q^0} \right] \frac{\partial}{\partial p_i} + \frac{\partial F}{\partial p_i} \frac{\partial}{\partial q^i} \qquad (61)$$

The infinitesimal transformation of the contact form

$$\alpha = dq^0 - p_i dq^i \qquad (62)$$

under this vector field can be calculated using

$$\mathcal{L}_V \alpha = d[i_V \alpha] + i_V d\alpha. \qquad (63)$$

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For us

$$i_{V_F}\alpha = -F, \quad d\alpha = -dp_i \wedge dq^i, \quad i_{V_F}d\alpha = \left[\frac{\partial F}{\partial q} + p_i\frac{\partial F}{\partial q^i}\right]dq^i + \frac{\partial F}{\partial p_i}dp_i. \quad (64)$$

It follows that

$$\mathcal{L}_{V_F}\alpha = -\frac{\partial F}{\partial q^0}\alpha. \quad (65)$$

Thus the vector field V_F changes the contact form only by an overall multiplication by a scalar: it leaves the contact structure unchanged. Such transformations are called Legendre transformations.

4.2   Characteristic Curves of a Function

Finite Legendre transformations can be constructed by composing such infinitesimal transformations; i.e., by determining the integral curves of this vector field.

Thus, a generating function defines a one-parameter family of Legendre transformations, determined by solving the Ordinary Differential Equations:

$$\frac{dq^i}{dt} = \frac{\partial F}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial F}{\partial q^i} - p_i\frac{\partial F}{\partial q^0}, \quad \frac{dq^0}{dt} = p_i\frac{\partial F}{\partial p_i} - F. \quad (66)$$

These are called the *characteristic curves* of the Generating Function F.

These equations are the analogues of Hamilton's equations in mechanics. But note that they are not quite the same: there are additional terms in $\dot{p}$ if the generating function depends on q^0. Moreover, the value of F is not always conserved:

$$\frac{dF}{dt} = -F\frac{\partial F}{\partial q^0}. \quad (67)$$

But if the initial value of F is zero, it remains zero.

Conversely, every hypersurface can be thought of as the set of zeros of some function F. The characteristic curves of F define a dynamical system on every hypersurface on a contact manifold. These curves are unchanged (up to reparametrization) by a change $F \to \phi(F)$ of the function defining the hypersurface. This dynamical system will play an important role in our approach to thermodynamics.

An important example of a Legendre transformation is one that interchanges a co-ordinate with its conjugate:

$$\tilde{p}_1 = q^1, \tilde{q}^1 = -p_1, \tilde{p}_2 = p_2, \tilde{q}^2 = q^2, \cdots \quad (68)$$

The characteristic curves of the function $F(p,q) = \frac{1}{2}[p_1^2 + (q^1)^2]$ are circles: the above Legendre transformation corresponds to a rotation through $\frac{\pi}{2}$.

4.3 Lagrange Brackets

The commutator of two vector fields satisfying the conditions $\mathcal{L}_V \alpha = g_V \alpha, \mathcal{L}_U \alpha = g_U \alpha$ is also an infinitesimal Legendre transformation. If the generating functions of U and V are F and G, what is the generating function of $[U,V]$? A straightforward calculation shows that it is given by the *Lagrange bracket*

$$\{F,G\} = G\frac{\partial F}{\partial q^0} - \frac{\partial G}{\partial q^0}F + p_i\left(\frac{\partial F}{\partial p_i}\frac{\partial G}{\partial q^0} - \frac{\partial F}{\partial q^0}\frac{\partial G}{\partial p_i}\right) + \frac{\partial F}{\partial p_i}\frac{\partial G}{\partial q^i} - \frac{\partial F}{\partial q^i}\frac{\partial G}{\partial p_i} \quad (69)$$

These brackets are different from Poisson brackets of mechanics in important ways. Although it defines a Lie algebra (i.e., antisymmetry and Jacobi identity are satisfied),

$$\{F,G\} = -\{G,F\}, \quad \{F,\{G,H\}\} + \{G,\{H,F\}\} + \{H,\{F,G\}\} = 0 \quad (70)$$

the Leibnitz rule of derivations is not satisfied in general:

$$\{F,GH\} - G\{F,H\} - \{F,G\}H = -GH\frac{\partial F}{\partial q^0} \neq 0. \quad (71)$$

Thus for example, even a constant can have non-zero brackets:

$$\{1,G\} = -\frac{\partial G}{\partial q^0}. \quad (72)$$

We have analogues of the canonical commutation relations

$$\{p_i, q^j\} = \delta^i_j, \quad \{q^i, q^j\} = 0 = \{p_i, p_j\} = \{q^0, q^i\}, \quad \{q^0, p_i\} = -p_i. \quad (73)$$

But due to violations of the Leibnitz identity these have to be used carefully. For example,

$$\{q^0, p_i q^i\} = 0. \quad (74)$$

4.4 Lagrangian Submanifold

A Lagrangian submanifold[12] of M is a submanifold of maximal dimension (i.e., n), *all of whose tangent vectors are annihilated by α* . As an example, the submanifold

$$p_1 = 0, \cdots p_n = 0, q^0 = \text{constant} \quad (75)$$

with co-ordinates $(q^1, \cdots q^n)$ is Lagrangian. But not every n-dimensional submanifold is Lagrangian. For example, the n-dimensional submanifold with co-ordinates $(p_1, q^1, q^3 \cdots q^n)$ for which

$$q^0 = \text{constant}, q^2 = \text{constant}, \quad p_3 = \cdots p_n = 0 \quad (76)$$

is not Lagrangian. The independent variables on the submanifold must have zero Lagrange bracket: they cannot include a conjugate pair. Thus a Lagrangian submanifold is the analogue of a configuration space in mechanics.

More generally, a submanifold is determined by a function Φ,

$$q^0 = \Phi(q^1, \cdots, q^n). \tag{77}$$

The remaining equations determining the submanifold are

$$p_i = \Phi_i(q^1, \cdots q^n), \quad \Phi_i = \frac{\partial \Phi}{\partial q^i}. \tag{78}$$

It is straightforward to verify that any infinitesimal variation within this surface satisfies $dq^0 - p_i dq^i = 0$, since

$$dq^0 = \frac{\partial \Phi}{\partial q^i} dq^i. \tag{79}$$

The trivial case of a Lagrangian submanifold mentioned above corresponds to the choice $\Phi = $ constant.

The same Lagrangian submanifold can have different descriptions, as we can use different canonical co-ordinate systems on the thermodynamics phase space. These different descriptions are related by Legendre transformations.

5 The Geometry of Thermodynamics

Now we turn to the formulation of thermodynamics in terms of contact geometry. As noted earlier, if a substance has n degrees of freedom, its thermodynamic phase space is $2n+1$ dimensional. The first law can be see as defining a contact structure on the thermodynamic phase space:

$$\alpha \equiv dq^0 - p_i dq^i = 0. \tag{80}$$

We can, as a first step, think of the 'co-ordinates' q^i as extensive variables and the 'conjugate momenta' p_i as the intensive variables. However as noted above, a Legendre transformation can mix these up. Having a picture that does not depend on the choice of co-ordinates in the thermodynamic phase space can be very useful in clarifying complicated thermodynamic relations. This is similar to the situation with canonical transformations in mechanics which allow momenta and co-ordinates to be mixed.

n the case of a gas, some of these equivalent descriptions, related by Legendre transformations, are

$$\begin{aligned}
\alpha &= dU - TdS + PdV \\
&= d\Xi + SdT + PdV, \quad \Xi = U - TS \\
&= dG + SdT - VdP, \quad G = U - TS + PV \\
&\sim dS - \frac{1}{T}dU - \frac{P}{T}dV.
\end{aligned} \tag{81}$$

Ξ is the *Helmholtz Free Energy* which is the convenient quantity to study a gas at constant temperature and volume. The *Gibbs Free Energy* G is useful to understand a gas at constant pressure and temperature.

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5.1 Equations of State≡Lagrangian Submanifold

The equations of state of a substance define a surface of dimension n in the thermodynamic phase space. Thus, among the $2n+1$ thermodynamic variables, there must be $n+1$ equations of state. But it cannot be any n-dimensional submanifold: *the equations of state of a substance must define a Lagrangian submanifold*. This is simply the condition that *any infinitesimal change in the state of the substance must satisfy the first law*. That is, any tangent vector field will annihilate α.

Once the 'fundamental relation' giving $q^0 = \Phi(q^1, \cdots q^n)$ is given, the remaining n equations of state follow by differentiation as above. As an example, for a gas, the internal energy as a function $u(s, v)$ of the other extensive variables give the other two equations of state:

$$T = \left(\frac{\partial u}{\partial s}\right)_v, \quad P = \left(\frac{\partial u}{\partial v}\right)_s \tag{82}$$

Thus each substance has a Lagrangian submanifold corresponding to it. But the same Lagrangian can have many descriptions in different canonical co-ordinate systems. The advantage of the geometric point of view is that it allows us to choose variables according to the convenience of the physical problem. Often, by a Legendre transformation we will be able to simplify equations that need to be solved. See below for examples.

5.2 Family of Substances→ Hamiltonian

A family of substances which have similar equations of state (e.g., van der Waals gases with various values of the parameters a, b) can be described by allowing the function Φ to also depend on n parameters $a_1, \cdots a_n$:

$$q^0 = \Phi(q^1 \cdots q^n | a_1, \cdots a_n). \tag{83}$$

These parameters could be quantities such as critical pressure and temperature.

We require the function defining such a family to satisfy a non-degeneracy condition:

$$\det \frac{\partial^2 \Phi}{\partial q \partial a} \neq 0. \tag{84}$$

The remaining equations determining the submanifold are

$$p_i = \Phi_i(q^1, \cdots q^n | a_1, \cdots a_n), \quad \Phi_i = \frac{\partial \Phi}{\partial q^i} \tag{85}$$

Given the non-degeneracy condition, we can eliminate the parameters $a_1 \cdots a_n$ from the above $n+1$ equations to get a single relation among the thermodynamic variables:

$$F(q^0, q^1 \cdots q^n, p_1, \cdots p_n) = 0 \tag{86}$$

We will see that this function $F(q, p)$ defines a dynamics on this hypersurface; by analogy to mechanics, we call this the *hamiltonian* of this family of substances.

There are some important differences from mechanics because the physics is determined by the set of zeros of F. A change of the hamiltonian $F \to \phi(F)$ by an invertible function $\phi : R \to R$ will leave the surface unchanged and the physics will be the same as well. However, adding a constant to F *will* change the physics, unlike in mechanics.

Thus the thermodynamics of a family of materials is described by a contact manifold $M, [\alpha]$ and a hyper-surface $F(q, p) = 0$ of co-dimension one on it.

Given one member of the family (e.g., ideal gas or paramagnet) is there a mathematical way of guessing the whole family? Unfortunately the answer is no. Such a generalization is essentially a postulate about on the macroscopic effects of the underlying microscopic system. Some physical input is needed to make the correct generalization. The arguments of van der Waals and Curie-Weiss were great theoretical leaps at a time when very little was known about molecules. Given a microscopic theory, we can in principle derive $\Phi(q|a)$ as an 'effective field theory'. In the absence of a microscopic theory, some mix of experimental information and physical intuition is needed.

Why do we define a family of substances to have exactly n parameters? With less than that many parameters, we are not talking of a 'generic' member. The non-degeneracy condition above cannot be satisfied and we would get a surface of co-dimension greater then one: it would not be defined by the vanishing of a single hamiltonian. On the other hand, with more than n parameters, we have the opposite problem: they cannot all be independent, as the surface is living in an ambient space of dimension only $2n + 1$. Thus in a sense additional parameters are 'irrelevant': they should not be important for the macroscopic dynamics of the system. Indeed in can der Waals theoy, exactly two parameters a, b give a good description of the non-ideal behavior of many gases.

5.3   The Hamilton-Jacobi Equation of a Family

Given the generating function $F(q, p)$ of a family of substances, we can recover the equations of state of each member of the family by solving the first order partial differential equation

$$F\left(q^0, q^1 \cdots q^n, \frac{\partial \Phi}{\partial q^1}, \cdots \frac{\partial \Phi}{\partial q^n}\right) = 0 \qquad (87)$$

The complete integral[3] of this equation will depend on n parameters $a_1, \cdots a_n$. The different equations of state of the family members are given materials by different choices of $a_1, \cdots a_n$. It is a fundamental tenet of Hamilton-Jacobi theory that *solving a first order PDE is equivalent to solving a system of ODEs for the characteristic curves.*

5.4 The Dynamics of Thermodynamics

Thus, given the generating function $F(q, p)$ of a family of substances, we get a dynamics on the hypersurface $F(q, p) = 0$. We get[4][3]

$$\frac{dq^i}{dt} = \frac{\partial F}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial F}{\partial q^i} - p_i \frac{\partial F}{\partial q^0}, \quad \frac{dq^0}{dt} = p_i \frac{\partial F}{\partial p_i} - F. \tag{88}$$

The parameters characterizing the material $a_1 \cdots a_n$ are given by the initial conditions of this dynamics. If we eliminate the 'time' variable we can get the complete integral of the Hamilton-Jacobi equation which in turn gives the equations of state.

It is tempting to speculate that this dynamics is related to the renormalization group evolution in quantum field theory: the thermodynamic phase space is 'theory' space, the coupling constants being the co-ordinates on it. Partial support for this conjecture is provided by the fact that the 'time' variable of our dynamics is related to (but is not always the same as) entropy.

5.5 The Characteristic Curves of the van der Waals gases

As an example,consider the case of the van der Waals family:

$$F(s, u, v, p_u, p_v) = \left[vp_v - up_u + \frac{3}{2} \right]^2 p_u^3 - \frac{27}{8} v^2 e^{-2s}. \tag{89}$$

The characteristic ODEs look quite formidable in these variables. There must be a change of variables in which the equations are simple to solve. Put first

$$\tilde{q}^0 = s + \frac{3}{2} \log v, \quad \tilde{q}^1 = v, \quad \tilde{q}^2 = uv \tag{90}$$

to simplify the formulas. The conjugates are given by comparing

$$ds - p_u du - p_v dv = dq^0 - \tilde{p}_1 d\tilde{q}^1 - \tilde{p}_2 d\tilde{q}^2 \Rightarrow \tilde{p}_1 = p_v + \frac{3}{2v} - \frac{u}{v}p_u, \quad \tilde{p}_2 = \frac{p_u}{v} \tag{91}$$

Then (after factoring out an overall $v^5 e^{-2\tilde{q}^0}$) the hypersurface can be described by the vanishing of

$$\tilde{F}(\tilde{q}^0, \tilde{q}^1, \tilde{q}^2, p_1, \tilde{p}_2) = e^{2\tilde{q}_0} \tilde{p}_1^2 \tilde{p}_2^3 - \frac{27}{8}. \tag{92}$$

Now we make one more change of variables

$$p_1 = e^{\frac{2}{5}\tilde{q}^0} \tilde{p}_1, \quad p_2 = e^{\frac{2}{5}\tilde{q}^0} \tilde{p}_2 \tag{93}$$

and choosing q^0, q^1, q^2 such that

$$\alpha \sim dq^0 - p_1 dq^1 - p_1 dq_2, \Rightarrow q^0 = \frac{5}{2} e^{\frac{2}{5}\tilde{q}^0}, \quad q^1 = \tilde{q}^1, \quad q^2 = \tilde{q}^2, \tag{94}$$

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[4]The equations in Ref.[3] don't have the term proportional to F. On the surface $F = 0$ our equations agree with theirs.

$$\tilde{F} = p_1^2 p_2^3 - \frac{27}{8}. \tag{95}$$

Because $\tilde{F}$ is independent of q^0, q^1, q^2 in these variables, p_1, p_2 are conserved quantities, and q^0, q^1, q^2 depend on 'time' t linearly: these are the 'normal coordinates' of the characteristic equations. Moreover from the homogeneity of $\tilde{F} + \frac{27}{8}$,

$$\frac{dq^0}{dt} = 5\frac{27}{8} \tag{96}$$

$$\frac{dq^1}{dt} = 2p_1 p_2^3, \quad \frac{dq^2}{dt} = 3p_1^2 p_2^2 \tag{97}$$

Transforming back to the original notation, we see that $v = q^1$ and $uv = q^2$ evolve linearly in 'time' t.:

$$v = q_0^1 + 2p_1 p_2^3 t, \quad uv = q_0^2 + 3p_1^2 p_2^2 t, \quad q^0 = 5\frac{27}{3}t \tag{98}$$

If we identify the constant of integration

$$q_0^1 = b, \quad q_0^2 = -a \tag{99}$$

and eliminate t we get

$$\frac{uv + a}{v - b} = \frac{3}{2}\frac{p_1}{p_2} = \frac{3}{2}\frac{\tilde{p}_1}{\tilde{p}_2} = \frac{3}{2}\frac{vp_v - up_u + \frac{3}{2}}{p_u} \tag{100}$$

Transforming to the original intensive variables,we get one form of the equation of state:

$$\begin{aligned}
\frac{uv + a}{v - b} &= \frac{\frac{3}{2}\frac{vP}{T} - u\frac{1}{T} + \frac{3}{2}}{\frac{1}{T}} \\
&= \frac{3}{2}[vP - u + \frac{3}{2}T] \tag{101}
\end{aligned}$$

Others forms follow similarly.

What is the meaning of the 'time' variable in this evolution, in terms of the original variable? We get (apart from a constant fixing the origin of t)

$$t = \frac{8}{5 \times 27}q^0 = \frac{4}{27}v^{\frac{3}{5}}e^{\frac{2}{5}s}. \tag{102}$$

The characteristic curves do not change if we replace t by any monotonic function of itself. Thus we can think of $s + \frac{3}{2}\log v$ equivalently as the time variable.

The thermodynamic 'time' variable is thus related to entropy, but is not exactly the same as it. Nevertheless, it seems reasonable to think of it as a measure of the coarse-graining of the underlying microscopic system.

6 Thermodynamics of a Black-hole

It is well-known[16] that a black hole has an entropy proportional to the area of its horizon. Einstein's equation imply that the total area of horizons cannot decrease as long as the source of gravity satisfies the positive energy condition (a weak form is sufficient).

The first indication of an analogy between thermodynamics and black holes was found in the work of Christodoulu and Ruffini [17] who were analyzing the Penrose process [19] of extracting energy from black holes. Beckenstein [20] and Hawking[21] showed that this was more than a mere analogy: black holes must have a temperature and an entropy when quantum effects are taken into account. For a recent review including a historical prespective, see Ref. [18].

Strominger and Vafa [22] have shown how to account for black hole entropy from string theory. Other approaches to involving loop quantum gravity[23], non-commutative geometry [24] are being vigorously pursued as well.

For simplicity let us restrict ourselves to spherically symmetric black holes. The metric can be brought to the form

$$ds^2 = V(r)dt^2 - \frac{dr^2}{V(r)} - r^2 d\Omega^2. \tag{103}$$

The horizon occurs when $V(r) = 0$. The temperature of this horizon is proportional to the acceleration of the null Killing vector, which works out to

$$\kappa = \frac{1}{2}V'(r_0) \tag{104}$$

The area of the horizon is, of course,

$$A = 4\pi r_0^2. \tag{105}$$

Einstein's equation of motion for the metric imply that any infinitesimal variation of these quantities are related by an analogue of the thermodynamic law:

$$dM = \frac{1}{8\pi}\kappa dA \tag{106}$$

where M is the mass of the black hole multiplied by Newton's constant. (In units where $c = 1$, this has dimensions of length.) Thus A is corresponds to entropy, temperature to $\frac{\kappa}{8\pi}$ and M to internal energy. This model of a black hole has one thermodynamic degree of freedom.

6.1 The Schwarzschild black hole

The simplest case, the Schwarzschild black hole, has

$$V(r) = 1 - \frac{2M}{r} \tag{107}$$

It has the two equations of state

$$\kappa = \frac{1}{4M}, \quad A = 16\pi M^2 \tag{108}$$

Note that

$$\frac{\kappa}{8\pi} = \frac{\partial M}{\partial A} = \left(\frac{\partial A}{\partial M} \right)^{-1} \tag{109}$$

as needed.

These equations of state are analogous to the ideal gas laws we discussed earlier. They describe a curve in the three dimensional thermodynamic phase space (M, A, κ). In order to find a Hamilton-Jacobi theory, we must depart from this ideal case by introducing some parameter the deforms Einstein's equation.

6.2 Schwarzschild-Anti de Sitter Family

The choice of such a deformation is a question of physics; the most obvious one physically is a cosmological constant.

If the cosmological constant is positive, even in the absence of mass there is a horizon; a black hole will have two horizons, with associated temperatures and entropies. Since our aim now is to keep things as simple as possible, we will choose the cosmological constant to be negative.

$$\Lambda = -\frac{3}{l^2}. \tag{110}$$

In the absence of mass the solution to Einstein's equations

$$R_{\mu\nu} - \frac{1}{2} g_{\mu\nu} = \Lambda g_{\mu\nu} \tag{111}$$

is the AdS (Anti de Sitter) metric

$$ds^2 = \left(1 + \frac{r^2}{l^2} \right) dt^2 - \frac{dr^2}{1 + \frac{r^2}{l^2}} - r^2 d\Omega^2; \tag{112}$$

i.e.,

$$V(r) = 1 + \frac{r^2}{l^2}. \tag{113}$$

This metric has no horizon as $V(r)$ never vanishes.

The spherically symmetric solution that has a horizon is

$$ds^2 = V(r) dt^2 - \frac{dr^2}{V(r)} - r^2 d\Omega^2 \tag{114}$$

where

$$V(r) = 1 - \frac{2M}{r} + \frac{r^2}{l^2}. \tag{115}$$

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The horizon radius r_0 is in 1-1 correspondence with the mass:

$$2M = r_0 + \frac{r_0^3}{l^2},\tag{116}$$

since they are both positive. The area of the horizon is

$$A = 4\pi r_0^2.\tag{117}$$

and the temperature is $\frac{\kappa}{8\pi}$, where

$$\kappa = \frac{1}{2}V'(r_0) = \frac{M}{r_0^2} + \frac{r_0}{l^2}.\tag{118}$$

We can now eliminate the cosmological constant to get the surface in the thermodynamic phase space describing the Schwarzschild-AdS black holes:

$$\left[3M - \frac{\kappa A}{4\pi}\right] = \sqrt{\frac{A}{4\pi}}.\tag{119}$$

and the Hamilton-Jacobi equation

$$\left[3M - 2A\frac{\partial M}{\partial A}\right] = \sqrt{\frac{A}{4\pi}}.\tag{120}$$

In this family, the Schwarzschild black hole has the largest entropy for a given mass. In this sense it is a kind of 'ground-state'. The solution of this differential equation depends on one constant of integration, which is the cosmological constant.

6.3   The Characteristic Curves of a Black hole

The above equation give the hamiltonian

$$F(M, A, p_A) = (3M - 2Ap_A) - \sqrt{\frac{A}{4\pi}}\tag{121}$$

Again, a Legendre transformation will simplify the dynamics. Put

$$A = 4\pi e^{2q}, q^0 = e^{-3q}M.\tag{122}$$

Then

$$dq^0 - pdq = 0 \Rightarrow p = e^{-3q}[2Ap_A - 3M].\tag{123}$$

After factoring out an overall factor of $-e^{3q}$ the Hamiltonian of the S-AdS black hole becomes:

$$\tilde{F}(q^0, q, p) = p + e^{-2q}.\tag{124}$$

The dynamical equations are, in these variables,

$$\frac{dq}{dt} = 1, \quad \frac{dp}{dt} = 2e^{-2q}, \quad \frac{dq^0}{dt} = -e^{-2t}.\tag{125}$$

The solution with $F = 0$ is

$$q = t, \quad p = -e^{-2t}, \quad q^0 = \frac{1}{2}e^{-2t} + a \tag{126}$$

where a is a constant of integration. Converting to the original variable $M = e^{3q}q^0$ and noting that $e^q = r_0$ we get the equation of state

$$M = \frac{1}{2}r_0 + ar_0^3. \tag{127}$$

Thus we identify the constant of integration with the cosmological constant.

$$a = \frac{1}{l^2} = -\frac{1}{3}\Lambda. \tag{128}$$

In this picture the 'time' variable of thermodynamic evolution is the logarithm of the entropy of the black hole.

In general a black hole can carry also angular momentum and electric charge. The family of such black holes will be described by deformations of Einstein-Maxwell equations at short distances. The obvious deformation of Maxwell's theory would be the Born-Infeld action. For the Einstein Lagrangian itself there are several higher derivative terms that can be added. But the analysis gets quite complicated as we have to solve for the black hole metric. It should be interesting however.

Finally, recall that the Hamilton-Jacobi formulation of mechanics gives the shortest route to quantum mechanics. We have considered elsewhere the possibility of a quantum thermodynamics[25].

7 Acknowledgement

References

[1] M. Born and E. Wolf *Principles of Optics* Cambridge University Press (1997)

[2] L. D. Landau and E. M. Lifshitz *Course of Theoretical Physics : Mechanics* and *Quantum Mechanics* Butterworth-Heinemann (1982)

[3] R. Courant and D. Hilbert, *Methods of Mathematical Physics* , Ch. II, Interscience Publishers (1962).

[4] J. W. Gibbs *Graphical Methods in the Thermodynamics of Fluids* in *Scientific Papers of J Willard Gibbs*, 2 vols. ed. by Bumstead, H. A., and Van Name, R. G., New York. Dover (1961).

[5] S. Chandrashekhar *An Introduction to the Study of Stellar Structure* New York, Dover (1967).

[6] R. K. Patria *Statistical Physics* Elsevier (1972); G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer *Thermodynamics* McGraw-Hill (1961)

[7] F. Mandl *Statistical Physics* Wiley (1971);A. Aharoni, Introduction to the Theory of Ferromagnetism (The International Series of Monographs on Physics)

[8] H. A. Buchdahl *The Concepts of Classical Thermodynamics*, Cambridge U. Press, London (1966);An Introduction to Hamiltonian Optics, Cambridge University Press (1970).

[9] M. Peterson, Am. J. Phys. 47,488 (1979)

[10] S. Omohundro *Geometric Perturbation Theory in Physics* World Scientific (1987)

[11] A. Mas-Colell, M. D. Whinston, J. R. Green *Microeconomic Theory* Oxford University Press, USA (1995)

[12] V. I. Arnold and A. B. Giventhal *Symplectic Geometry* in Vol. IV of *Encyclopedia of Mathematical Sciences* ed. by V. I. Arnold and S. P. Novikov, Springer (2001)

[13] D. E. Blair, *Contact Manifolds in Riemannian Geometry* Lecture Notes in Mathematics, 509, Springer (1976).

[14] J. L. Sengers, *How Fluids Unmix: Discoveries by the School of Van der Waals and Kamerlingh Onnes*, Royal Dutch Academy; available online at http://www.knaw.nl/waals/book.html.

[15] R. de Bruyn Ouboter, Physica 154, 42-55 (1988).

[16] R. M. Wald *General Relativity* University Of Chicago Press (1984); the more recent paper M. M. Akbar, hep-th/0401228 was also useful.

[17] D. Christodoulu, Phys. Rev. Lett. **25** 1596 (1971); D. Christodoulu and R. Ruffini, Phys. Rev. **D4** 3552 (1971).

[18] T. Damour, "The entropy of black holes: a primer" arXiv:hep-th/040160.

[19] R. Penrose, *Rivista Nuovo Cimento* **1**, 252 (1969);
R. Penrose and R.M. Floyd, *Nature* **229**, 177 (1971).

[20] J.D. Bekenstein, *Lett. Nuovo Cimento* **4**, 737 (1972); *Phys. Rev.* **D7**, 2333 (1973).

[21] S.W. Hawking, *Nature* **248**, 30 (1974); *Comm. Math. Phys.* **43**, 199 (1975).

[22] A. Strominger and C. Vafa, Phys. Lett. B **379**, 99 (1996) [arXiv:hep-th/9601029].

[23] A. Ashtekar, J. Baez, A. Corichi and K. Krasnov, *Phys. Rev. Lett.* **80**, 904 (1998); A. Ashtekar, J.C. Baez and K. Krasnov, *Adv. Theor. Math. Phys.* **4**, 1 (2000).

[24] S. Ansoldi, P. Nicolini, A. Smailagic and E. Spallucci, Phys. Lett. B **645**, 261 (2007) [arXiv:gr-qc/0612035].

[25] S. G. Rajeev, arXiv:math-ph/0703061. To appear in Ann. Phys.